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(54) Thermoset acrylic resin composition for coating metallic materials and stainless steel coated with the composition.

(57) A thermoset acrylic resin composition for coating metallic materials, particularly stainless steel, having a superior adhesion thereonto and hence giving superior resistance to forming after coating, and a stainless steel piece coated with a coating material comprising the above composition, followed by baking, and having a superior colourability and endurability, are provided, which compositions is obtained by radical-copolymerizing (a) 40 to 80% by weight an acrylic or methacrylic acid ester having 1 to 12 C in the ester moiety, (b) 20 to 5% by weight a hydroxyl group- or epoxy group-containing acrylic or methacrylic acid ester, (c) 20 to 0.01% by weight a vinyl group-containing polysiloxane and (d) 20 to 2% by weight a vinyl group-containing silane compound, these % by weight being based on the total weight of monomers (a) to (d).

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Thermoset acrylic resin composition for coating metallic materials and stainless steel coated with the composition

This invention relates to an acrylic resin composition for coating metallic materials. More particularly it relates to such a composition obtained by copolymerizing a specified acrylic acid ester or methacrylic acid ester, a vinyl group-containing polysiloxane and a vinyl group containing silane compound. This invention further relates to a decorative stainless steel piece coated with the modified acrylic resin.

Known thermoset acrylic resin compositions have been broadly used as coating materials for various metals such as iron, aluminium, copper and stainless steel since the compositions afford a coating which is superior in lustre, transparency, hardness, weather resistance, chemical resistance and other properties. However, the resultant coating often has insufficient adhesion to metals; hence it does not to endure shaping-processing such as bending through 0 ~ 2 to 180°. In order to impart such a bending resistance to the coating, it is necessary with the thermoset acrylic resin composition to blend an agent for imparting bending resistance. However, such a blending is usually

accompanied by reduction in at least one of the physical properties such as hardness, chemical resistance, hot water resistance and other properties of the above coating. Thus, in order to avoid such reduction in physical properties and yet obtain a bending-processed, formed product coated with a thermoset acrylic resin composition, it is the present state of the art that the bending-processed, formed product is post-coated with the resin composition.

However, if a coating meterial (a thermoset acrylic resin composition) were available which would endure the above bending processing after coating, then it would be possible to produce various fabricated products such as domestic appliances, office machines, building materials, etc, by the use of the so-called precoat sheet obtained by coating such a coating material onto metallic sheets. When such a precoat sheet is utilized, it is possible to remove technical difficulties at the time of coating, make the operational environment non-pollutive and effect energy-saving, as compared with the case where individual formed products are coated. Hence the desire for the coating material which endures the bending processing.

Furthermore, stainless steel materials, particularly stainless steel sheet, steel band, steel pipe, etc,

surface-adjusted by BA (Bright Annealing), buffing, hairline polishing, etc, so as to retain their planar surfaces are characterized by endurability and metallic lustre. Hence these forming-processed products have been broadly used for interior and exterior parts for automobiles using trim, emblem, stainless foil, etc, for automobiles, interior and exterior building materials, furniture, domestic appliances, etc. However, such stainless steel materials, even if surface-adjusted, have raised problems in that the products are liable to cause rust or contamination, and the shade of the steel materials is limited to the colour only of the steel steel itself, and thus they are restricted in the aspect of decorative properties.

For the purpose of decoration, rust prevention and contamination prevention of stainless steel materials, the materials sometimes are coated with an acrylic resin paint while making the most of the metallic lustre of stainless steel. However, in the case where the coating formed from such a paint is required to have transparency and high hardness, the softness and adhesion are instead sacrificed. Thus when such a stainless steel material having a high hardness coating is subjected to forming such as press processing or roll processing, it raises drawbacks in that cracks occur on the coating or the coating peels off. Further, since

such a coating is insufficient in salt resistance, alkali resistance and weather resistance, the uses of stainless steel materials having the high hardness acrylic resin coating have been resistricted to indoor uses where the quantity of UV light is small.

As to the colouration of the surface of the stainless steel materials, there is a method of forming a coating having a thickness of from 500 to 10000 Å by way of anodic oxidation on the surface of the materials, to develop colour on the surface through interference of natural light and reflected light (which method will hereinafter be abbreviated to as "oxidation method"). However, the steel materials according to this colour development method have the following drawbacks: discolouration of the processed surface of stainless steel materials, change in colour tone depending on the direction of view of adhesion of oil or the like and high production cost due to the treating technique. Thus this method has been adopted only for extremely restricted uses. Accordingly, it has been practically very difficult to effect a transparent colouration on the surface of stainless steel materials while retaining the metallic lustre of the materials thereon and at the same time impart rust resistance.

In view of the foregoing technical situations, the

present inventors have made extensive research in order to find a thermoset acrylic resin composition having superior forming processability after coating, and as a result have found that copolymer compositions obtained by subjecting to radical copolymerization, (a) an alkyl acrylate or an alkyl methacrylate, (b), a hydroxyl group or epoxy group-containing acrylic acid ester, (c) a vinyl group-containing polysiloxane and (d) a vinyl group-containing silane compound, each having a definite range of carbon atoms and in definite amount, are more suitable for attaining the above-mentioned objects.

Further the present inventors have made extensive research in order to solve the problems of the prior art relative to stainless steel materials, and as a result have found that when a coating material comprising a silicone resin-modified acrylic resin as an active ingredient is coated on stainless steel materials, followed by baking, then there is obtain a siloxane bond-containing resin coating on the surface of the materials. Further it has been found that this coating typically does not have the above various drawbacks due to conventional acrylic resin coating materials; it is possible to blend a pigment which can bring about a desired colouration; and there is no defect in the above coating by way of anodic oxidization.

As is apparent from the foregoing, an object of the present invention is to provide a thermoset acrylic resin composition for coating metals which can be formulated to cause neither peeling-off nor blushing due to bending processing to be usable for coated metal sheets.

Another object of the present invention is to provide a decorative stainless steel piece coated with a modified acrylic resin, having a superior colourability and endurability.

The present invention provides a thermoset acrylic resin compoosition for coating metallic materials, obtained by subjecting to radical copolymerization, the following monomers (a) to (d), with the proportions by weight being based on the total weight of the monomers (a) to (d):

(a) at least one compound selected from the group consisting of acrylic acid esters and methacrylic acid esters, the esters having 1 to 12 carbon atoms in the ester group moiety, in a proportion of 40 to 80% by weight;

(b) at least one compound selected from the group consisting of hydroxyl group- or epoxy group-containing acrylic acid esters and hydroxyl group- or epoxy group-containing methacrylic acid esters; in a

proportion of 20 to 5% by weight;

(c) a vinyl group-containing polysiloxane, in a proportion of 20 to 0.01% by weight; and

(d) a vinyl group-containing silane compound, in a proportion of 20 to 2% by weight.

0.1 to 5% by weight of an organic acid having 3 or more carbon atoms can be further blended with the mixture of said monomers, either as the acid itself or in the form of an anhydride or other derivative, and especially acrylic acid or malic anhydride.

The copolymer obtainer by the radical copolymerization preferably has a weight average molecular weight of 5,000 to 300,000.

The vinyl group-containing polysiloxane is preferably at least one compound selected from the group consisting of the following monomers (e) to (h):

(e) vinyl group-terminated polyalkylsiloxanes having a viscosity at 25°C (η) of 2 to 100,000 cp and the following structural formula:

$$CH_2=CH-\underset{CH_3}{\overset{CH_3}{Si}}-O-(-\underset{CH_3}{\overset{CH_3}{Si}}-O\,)_n\,\underset{CH_3}{\overset{CH_3}{Si}}-CH=CH_2$$

wherein n represents a positive integer;

(f) polydimethyl-polymethylvinylsiloxane copolymers having a η of 10 to 100,000 cp at 25°C and the following structural formula:

$$(CH_3)_3\,Si-O-\left(-\underset{CH_3}{\overset{CH=CH_2}{Si}}-O-\right)_m\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right)_n\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right)Si(CH_3)_3$$

wherein m and n each represent a positive integer;

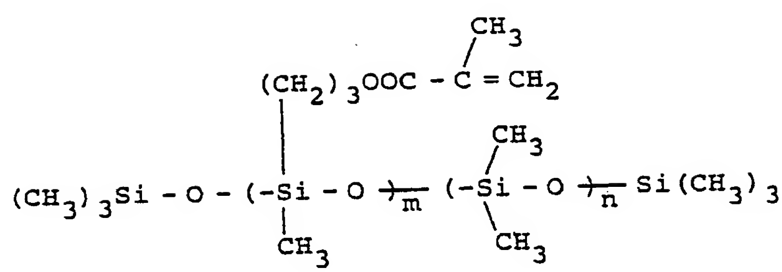
(g) methacryloxypropyl group-terminated polydimethylsiloxanes having a η of 5 to 100,000 cp at 25°C and the following structural formula:

$$CH_2=\underset{CH_3}{C}-COO(CH_2)_3\,\underset{CH_3}{\overset{CH_3}{Si}}-O-\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right)_n$$

$$-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2\;CH_2\;CH_2OOC\underset{CH_3}{C}=CH_2$$

wherein n represents a positive integer;

(h) polydimethyl-methacryloxyproplysiloxanes having a η of 10 to 100,000 cp at 25°C and the following structural formula:



wherein n represents a positive integer; and compounds having a phenyl group substituted in part for $-(CH_3)_2$ in $Si(CH_3)_2$ in (e) to (h).

The present invention further resides in a stainless steel piece having thereon a coating comprising a modified acrylic resin as an active ingredient, prepared by subjecting to radical copolymerization, (1) 20 to 2% by weight of vinyl group-containing alkoxysilane, (2) 20 to 0.01% by weight of a vinyl group-containing polysiloxane, (3) 20 to 5% by weight of a hydroxyl group-or epoxy group-containing acrylic acid ester or methacrylic acid ester and 40 to 80% by weight of (4) an acrylic acid ester having 1 to 12 carbon atoms in the ester croup moiety or (5) a methacrylic acid ester having 1 to 12 carbon atoms in the ester group moiety, in the presence of 0.1 to 5% by weight of an organic acid having 3 or more carbon atoms, the respective % by weight being based on the total weight of the monomers (1) to (5), and baking at a temperature of 100 to 350°C.

The stainless steel piece suitably has a coating with a thickness of 1 to 30 µ.

A pigment having an average particle diameter of 2 µ or less can be present in the coating. The coating can be baked again after forming-processing at a temperature of 100 to 300°C.

The composition of the present invention is obtained by subjecting monomers of the four groups (a) to (d) to radical copolymerization.

For the compounds of group (a), acrylic acid esters having 1 to 12 carbon atoms in the ester group moiety or methacrylic acid esters having 1 to 12 carbon atoms in the ester group moiety are used in a proportion of 40 to 80% by weight based on the total weight of the monomers (a) to (d). Concrete examples of these esters are acrylates such as ethyl acrylate or butyl acrylate and methacrylates such as methyl methacrylate, ethyl methacrylate or butyl methacrylate. If these acrylates or methacrylates have 13 or more carbons in the alkyl group moiety, the physical properties thereof as a coating material relative to final products are often insufficient. This applies also to the case where the amounts employed are less than 40% by weight or exceed 80% by weight.

Next, for the compounds of group (b), hydroxyl group- or epoxy group-containing acrylic acid esters or hydroxyl group- or epoxy group-containing methacrylic acid esters are used in a proportion of 20 to 5% by weight based on the total weight of monomers used for the composition. Concrete examples of these esters are 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and glycidyl acrylate, 2-hydroxyethyl methacrylate and glycidyl methacrylate. If the proportion of the compounds of group (b) exceeds 20% by weight, there is a fear that the physical properties of the coating prepared from the resulting final composition are inferior, while if it is less than 5% by weight, the curability of the final composition is often insufficient.

Next, for the compounds of group (c), vinyl group-containing polysiloxanes are used in a proportion of 20 to 0.01% by weight based on the total weight of the monomers used for the composition. The vinyl group may be bonded in the form of the terminal group of the polysiloxanes or may be bonded indrectly to Si atom in the repeating units of the polysiloxanes or bonded thereto by the medium of another functional group. If the proportion of the polysiloxanes used exceeds 20% by weight, the resulting coating is too soft and also poor in adhesion, while if it is less than 0.01% by weight,

the physical properties of the coating are insufficient. Concrete examples of the polysiloxanes are the compounds (e) to (h) described above. The η of the compounds is the ranges given above.

Finally, as for the compounds of group (d), vinyl group-containing silane compounds are used in a proportion of 20 to 2% by weight based on the total weight of the monomers used for the composition. The silane compounds have two or three hydrolyzable functional groups bonded directly to the Si atom besides the above vinyl group. While these functional groups are not limited, alkoxy groups having 1 to 4 carbon atoms are easily used and afford preferred results. Concrete examples of such vinyl group-containing silane compounds are vinyltrimethoxysilane, vinyltriethoxysilane, vinyldimethoxyethoxysilane, methylvinyldimethoxysilane, methylvinyldiethoxysilane, γ-methacryloxypropyltrimethoxysilane and γ-methacryloxypropylmethyldimethoxysilane.

The above monomers of groups (a) to (d) are suitably copolymerized in the pesence of a radical-generating agent. While the form of the copolymerization is not limited, solvent polymerization in the presence of a solvent is easily conducted and affords good results. Examples of such solvents are aromatic hydrocarbons such

as toluene or xylene, ketones such as methyl ethyl ketone or acetone, and alcohols such as n-butanol or cyclohexanol. The kind of the radical-generating agent and the proportion thereof are similar to those in the case of polymerization of usual acrylic acid esters or methacrylic acid esters. For example, a radical-generating agent such as benzoyl peroxide or azobisisobutyronitrile can be used in a proportion of 0.2 to 2% by weight based on the total weight of the monomers for the composition, and the copolymerization carried out at a temperature of 60° to 120°C, depending on the half-life of the agent. In the copolymerization, the total amounts of the monomers of the four groups may be mixed together at the time for copolymerization, or a part of the monomer mixture may be additionally fed to other monomers or the monomer mixture during the copolymerization.

As to the extent of the polymerization of the acrylic resin composition of the present invention, the composition is preferred to have a viscosity at 25°C of 100 to 2,000 cp, preferably 150 to 1,000 cp in the case of xylene solvent and a resin content of 40% by weight. The copolymers within this viscosity range have a weight average molecular weight in the range of 5,000 to 30,000 in terms of values according to gel permeation chromatography. The adjustment of polymerization degree

is carried out depending on the quantity of radical-generating agent or chain transfer agent used, as in the case of production of usual acrylic resins. If the above viscosity is less than 100 cp, unpolymerized monomers are liable to remain, and since the viscosity of the composition is too low, its operability as coating material can not be regarded as good, while if the viscosity exceeds 2,000 cp, then due to its too high viscosity, the operability is not only inferior, but also there is a tendency that the hot water resistance and corrosion resistance of the resulting coating is lower.

In the above manner, a copolymer as the thermoset acrylic resin composition of the present invention for coating metallic materials is obtained. The solvent used at the time of copolymerization may be left in the resulting composition as it is, or may be recovered by heating under reduced pressure or the like means, together with recovery of the unreacted monomers of the above groups (a) to (d).

The acrylic resin composition of the present invention may be subjected to crosslinking reaction for thermosetting, by utilizing the functional group contained in the compounds of group (b). As the crosslinking agent or reaction promotor therefor, organic acids or organic base compounds for instance as

described below can be used in a proportion of 0.1 to 5% by weight, preferably 0.5 to 3% by weight based on the weight of the acrylic resin composition.

Concrete examples of such organic acids are acrylic acid, methacrylic acid, phthalic acid, maleic acid or p-toluenesulphonic acid. Acrylic acid or methacrylic acid may be added at the same time as copolymerization for producting the acrylic resin composition of the present invention and copolymerized. Other organic acids are added after preparation of the composition.

Examples of the above organic base compounds are benzyldimethylamine, polyamines, polyamides, etc, which are used as a catalyst for epoxy group ring opening relative to the compounds of group (b). However, certain amino group-containing silane compounds may be more preferably used, such as γ-aminopropyltriethoxysilane, 3-(2-aminoethyl)aminopropyltrimethoxysilane, or 3-(2-aminoethyl)aminopropylmethyldimethoxysilane. These organic base compounds are added and mixed after preparation of the acrylic resin composition of the present invention. Examples of other curing promotors are bases, salts or acids such as potassium hydroxide, tetramethylammonium hydroxide, sodium acetate, phosphoric acid, toluenesulphonic acid. However, from the viewpoint of the chemical stability of the catalyst

itself, organometallic compounds such as dibutyltin oxide or tetrabutyl tin may be preferably used.

When the composition of the present invention is used as the coating material for coating metals, various kinds of auxiliary agents blended in paints of similar kinds of resins may be used, such as an organic or inorganic pigment, dyestuff, UV light absorber, dispersing agent, sagging-prevention agent, etc. As to the above dyestuff and pigment, if importance is attached to the weather resistance of the coating, the use of pigment is preferred. Further if importance is attached to the transparency of the coating coloured by pigment addition, pigment particles are preferably ground into finely-divided particles of 2 µ or less, preferably 1 µ or less, by various kinds of paint shakers such as ball mill, centrimill, sand grind mill, and the particles are dispersed in the coating material and used. The fact that the coating material of the present invention has a good pigment-dispersibility is one of its specific features. If transparency is not particularly required, a pigment for general purpose may be dispersed, as it is, in the coating material. Further, in order to improve the coating operability or finishing properties, a solvent such as xylene, butyl acetate, ethylcellosolve, butanol or 2-butanone may be blended in a suitable amount.

As for the method for coating the metal surface with the coating material of the composition of the present invention, any of the conventional methods may be employed such as curtain flow coating, roll coating, spraying, dipping, etc. The resulting coating typically has a thickness as extremely low as 2 to 15 μ, and nevertheless its specific features can be fully exhibited after curing described later.

The product of the present invention which is a thermoset silicone-modified acrylic resin composition, can be cured by heating after formation of the coating. The coating is suitably cured at 150 to 280°C, preferably 200 to 270°C and in a short time such as 1 to 30 minutes, preferably 3 to 15 minutes. Another curing method is the following low temperature curing:

The coating of the composition of the present invention contains an alkoxysilane and a reaction promotor such as or organic acid or organic base, and crosslinking reaction gradually proceeds even at low temperature such as room temperature to 60°C; hence such a low temperature curing method can be easily utilized for woodworking, for repairing building structures or automobiles or for other purposes.

When the acrylic resin composition of the present invention is used as the coating, a coating having a high degree of crosslinking is readily obtained, and this coating is superior in adhesion and processing-resistance notwithstanding its high hardness. The reason is presumed to consist in the following three points:

(1) When the blending ratio of acrylic acid ester or methacrylic acid ester to the vinyl group-containing polysiloxane both as raw materials for the acrylic resin composition, and the polymerization degree of the composition copolymer are adequately selected, ultimately the flexibility and hardness of the coating can be adequately retained.

(2) The vinyl group-containing silane compound as one of the copolymerization components forms siloxane bond, bond to hydroxyl group and chemical or physical bond to metals to be coated.

(3) The organic acid or organic base compound added to the composition promotes crosslinking reaction.

The present invention in one aspect relates to a stainless steel material having a cured coating comprising siloxane bonds as its skeleton, formed by

coating material mainly of a silicone-modified acrylic resin, followed by thermosetting.

As to the stainless steel used, its composition and surface-adjustment method have no particular limitation. However, in order to assure the adhesion of the coating, dirts such as oil matters, dusts, etc, are preferably removed by washing in advance, as described later.

The modified acrylic resin coating material of the present invention may be naturally applied also to steel materials or aluminium materials. Nevertheless, the coating of the present invention is best limited to stainless steel materials in that none of general coatings including known acrylic resin coatings could have fully satisifed all of weather resistance, rust prevention, hardness and adhesion relative to stainless steel materials.

Products of stainless steel materials have generally been surface-adjusted. As the methods therefore, for example, BA (Bright Annealing), 2B (annealing and acid washing followed by being subjected to skinpass roll), buffing, hairline polishing (HL), etc, have been conducted.

For the stainless steel materials used in the present invention, the above surface-adjustment is not indispensable. However, if dirt such as oil matters, dusts, etc, are attached to the surface of the materials, at the time of adjustment or preservation of the materials prior to coating, then it is preferred to carry out degreasing and washing (e.g. solvent washing with trichlene or the like) or alkali washing. As to the method of coating with the modified acrylic resin of the present invention, it is possible employ for instance any of roll coater method, blade coater method, gravure coater method, beat coater method, curtain flow coater method, dip coater method, and spray coater method. As an example, roll coater apparatus is illustrated in Fig. 1.

Fig. 1 shows a roll coater apparatus as an example of the coating apparatus used in the present invention.

In this figure, the apparatus includes payoff reel 1; welding machine 2 for connecting coils; accumulator 3; pretreating means 4 for degreasing and washing; No. 1 roll coater 5; No. 2 roll coater 6; No. 1 baking furnace 7; No. 2 baking furnace 8; cooling means 9 after coating and baking; cutter 10; coil winder 11 after completion of coating and baking; and coil 12 to be coated.

The above apparatus is an apparatus wherein a bandform steel sheet is continuously coated and baked, and No. 1 roll coater (5) and No. 1 baking furnace (7); and No. 2 roll coater (6) and No. 2 baking furnace (8) are paired, respectively, that is, the so-called 2 coats and 2 bakes are possible.

When the coating and baking in the present invention are carried out using the apparatus, the above No. 2 roll coater (6) is not always required.

In short, band-form stainless steel sheets 12 fed from payoff reel 1 are continuously connected by welding machine 2, and degreased with an alkali and washed by pretreating means 4 in advance of coating, followed by coating coil to be coated 12 by No. 1 roll coater 5 so as to give a desired thickness of coating, baking in No. 1 baking furnace 7 and No. 2 baking furnace 8, cooling at cooling means 9, cutting by cutter 10 into coil units and winding up by coil winder 11.

As to the baking conditions, i.e. thermosetting conditions, temperature and time are in a relative relationship and also the conditions vary depending on the properties of coating required. However, the baking is possible in a temperature range of 100° to 350°C and in a broad period range of one hour to 0.5 minute.

Preferable baking conditions under which baking is more easily carried out are those under which the material to be coated is baked for a relatively short time of 1 to 10 minutes in an atmosphere heated to 150° to 300°C. However, conditions under which the heating time is somewhat prolonged, e.g. heating at 150° to 250°C for 10 to 60 minutes, make it possible further to improve the properties of the coating of the present invention.

The above fact also means that when coated band-form steel or the like of the present invention is brought into mass production, it is possible to improve the properties of the coating by re-baking after baking as follows:

For example, when a coated stainless steel material first baked at 250°C for 1 to 5 minutes is reheated e.g. to 220°C for 20 minutes, it is possible to produce the steel material having further improved properties without harming mass-productivity.

The thickness of the coating of the present invention is preferably in the range of 1 to 30 μ. If it is less than 1 μ, an interference fringe is observed on the surface of the coating; this is often undesirable in respect of appearance. On the often hand, if the thickness exceeds 30 μ, the properties of the coating

are not usually improved, and, to the contrary, when the stainless steel materials are subjected to a great extent of processing, there is tendency that the coating is liable to peel off.

The characteristic effectiveness of the present invention is in that even when the coating is extremely thin, a sufficient corrosion resistance can be exhibited. Namely, in the case of coatings formed by general paints, unless the coating has a considerable thickness e.g 30 μ or more, there is the a drawback that a coating-deficient part is liable to occur, whereas in the case of the present invention, even when the thickness of the coating is only several μ as above, it is normally possible to retain the properties of coating.

In the present invention, as has been described above in details, since a specific coating of organic and inorganic substances is formed on the surface of a stainless steel piece, the resulting product of the present invention has the following specific features as compared with conventional acrylic resin coating or anode-oxidized coating:

(1) Since the coating is superior in pigment-dispersibility, excellent transparency is easily obtained and a lustrous colouration of stainless steel tone is exhibited.

(2) Since the coating has a surface hardness as high as 2H or more, it is hardly injured.

(3) The coating has a superior weather resistance.

(4) The coating has a superior adhesion.

(5) The coating has a good corrosion resistance.

(6) The coating has a good chemical resistance.

(7) Through roll processing, press processing, etc, the coating does not peel off.

(8) The colour tone does not vary depending on the direction of view.

(9) The coating is superior in resistance to fingerprint contamination and resistance to oil contamination.

(10)It is possible to prepare the coating economically.

Due to the above specific features, the present invention makes it possible to extend the degree of freeedom of design relative to colour specification of coating materials, to a larger extent than conventional products. Further, since it is possible to subject stainless flat sheet or coil after surface-treatment, to forming-processing, various effects on the final product are obtained such as energy saving, reduction in rejection rate, reduction in cost, etc.

Next, the present invention will be described in more detail by way of non-limiting Preparation Examples and Use Examples.

Preparation example 1

Methyl methacrylate (50 parts by weight; the succeeding parts being all by weight), butyl methacrylate (10

parts), glycidyl methacrylate (20 parts), acrylic acid (2 parts), vinyl-terminated polydimethylsiloxane ($n = 50$) (10 parts) and γ-methacryloxypropyltrimethoxysilane (10 parts) were dissolved in xylene (150 parts), and benzoyl peroxide (one part) was added, followed by reacting the mixture in nitrogen stream at 100°C for 4 hours, to obtain a silicone-modified acrylic polymer having a viscosity at 25°C of 210 cp, indicated in Table 1.

<u>Preparation examples 2 ~ 8</u>

Preparation example 1 was repeated except that the components and composition were varied, to obtain silicone-modified acrylic polymers having viscosities at 25°C indicated in Table 1.

<u>Use examples 1 ~ 6 and Comparative examples 1 ~ 2</u>

The respective polymers obtained in Preparation examples 1 ~ 8 were diluted by the equal weight of a mixed solvent of xylene-butanol (2 : 1), applied onto a stainless steel sheet (SUS 430, planished) and subjected to heat setting at 230°C for 5 minutes to obtain coatings of 5 ~ 6 μ thick, followed by evaluation. The results are shown in Table 2.

Table 1

	Preparation example	1	2	3	4	5	6	7	8
a	MMA	50	40	50	60	50	30	60	50
	BMA	10	10				20	10	
	EA		10						
	LMA			10		20	20		20
b	GMA	20	10	10		20	20	20	20
	HEMA		10		10				
c	Vinylpolysiloxane	10	10		20	1	0.1	20	
	Methacrylpolysiloxane			10					
d	MOPS-U	10		10	10	10	10		10
	VTS-U		10						
	Acrylic acid	2	1			1	1	1	1
	Maleic acid			2	1				
	BPO	0.5	0.5	0.5	0.5	1	1	0.5	0.5
	Xylene	150	150	150	150	150	150	150	150
	Solution viscosity (25°C)	210	385	190	220	420	530	240	310

Note: MMA: Methyl methacrylate

BMA: n-Butyl methacrylate

EA : Ethyl acrylate

LMA: Lauryl methacrylate

GMA: Glycidyl methacrylate

HEMA: 2-Hydroxyethyl methacrylate

Vinylpolysiloxane: Vinyl-terminated polydimethylsiloxane ($\eta = 50$)

Methacrylpolysiloxane: Methacryloxypropyl-terminated polydimethylsiloxane ($\eta = 200$)

MOPS-U: Methacryloxypropyltrimethoxysilane

VTS-U: Vinyltrimethoxysilane

Table 2

	Use example						Comparative example	
	1	2	3	4	5	6	1	2
Preparation example No.	1	2	3	4	5	6	7	8
Pencil hardness	2H	3H	2H	2H	3H	3H	B	2H
Adhesion	○	○	○	○	○	○	×	○
Processability (at 180°C)	○	○	○	○	○	○	○	×
Anticorrosion (SST 200 hr)	○	○	○	○	○	○	Δ	○
Hot water resistance	○	○	○	○	○	○	×	○

In the above Table 2, the evaluation methods are as follows:

Judgement: o No change in appearance was observed.

Δ Changes (cracks, blushing, etc.) were somewhat observed.

× Changes (cracks, blushing, etc.) were clearly observed.

Pencil hardness: Measured according to JIS-K-5400.

Adhesion: After cross-cut adhesion test according to JIS-K-5400, peel test was five times carried out with cellophane tape.

Processability: Test piece was folded by 180° with a vise and folded part was judged with naked eyes.

Corrosion resistance: Test piece was subjected to cross-cut and bending processings (2 ϕ 180° folded), followed by saline solution spray test (according to JIS Z 2371) for 200 hours to observe appearance change such as occurrence of rust, blister, etc.

Hot water resistance: Test piece was cross-cut and immersed in boiling water for 2 hours, followed by cellophane tape peel test.

Next, Coating material preparation examples directed to the second aspect of the present invention will be described.

Coating material preparation examples 1-1 and 1-2

Methyl methacrylate (40 parts by weight; the succeeding parts being all by weight), n-butyl methacrylate (10 parts) and ethyl acrylate (10 parts) (the total of the above parts: 60 parts) were mixed with glycidyl methacrylate, 2-hydroxyethyl methacrylate, a two vinyls-terminated dimethylpolysiloxane (viscosity: 50 cp) and methacryloxypropyltrimethoxysilane, each 10 parts, as modifying monomers, and acrylic acid (0.5 part) and benzoyl peroxide (0.5 part), to prepare a mixed solution of monomers for polymerization. This mixed solution was dropwise added to xylene (150 parts) kept at 100°C to effect copolymerization reaction and thereby finally obtain a silicone resin-modified acrylic resin solvent solution having a solution viscosity at 25°C of 340 cp (resin concentration: 40% by weight).

To this solution was added a mixed solvent of xylene-butanol (ratio by weight, 1 : 1) to make the resin content 30%, followed by adding a UV light absorber (0.5% by weight based on the resin content), and further adding and mixing either one of the following two kinds of coloring pigments (each 2.5% by weight based on the resin content):

Transoxide Red (tradename of product made by Dainichi Seika Kogyo Company) having a particle diameter of 1 u or

less (Coating material preparation example 1-1) (a red coating material was obtained); and

Cyan Blue-5050 (tradename of product made by Dainichi Seika Kogyo Company) having a particle diameter of 1 μ or less (Coating material preparation example 1-2) (a blue coating material was obtained).

Coating material preparation examples 2-1 and 2-2

Preparation of a mixed solution of monomers for polymerization, and copolymerization reaction were carried out under the same conditions as in coating material preparation examples 1-1 and 1-2 except that as the monomers for copolymerization, lauryl methacrylate (19 parts) was used in place of ethyl acrylate and two methacryls-terminated dimethylpolysiloxane (one part, viscosity 200 cp), in place of two vinyls-temrinated dimethylpolysiloxane, to obtain a silicone resin-modified acrylic resin solvent solution having a solution viscosity at 25°C of 600 cp.

To this solution were added solvent, UV light absorber and pigment in the same manner as in coating material preparation examples 1-1 and 1-2 to obtain a red coating material and a blue one.

Use examples 7 ~ 13 and Comparative examples 3 ~ 4

The coating of the present invention was baked on a stainless steel sheet under various conditions indicated in the following Table 3 and according to the notes

described below the Table, followed by evaluating the properties of the resulting coatings for comparison.

Table 3

Experiment No.	Coating thickness μ	Setting conditions °C, min.	Pencil hardness	Color tone	Cross-cut, Erichsen's peeling
Compar. ex. 3	0.5	300, 1	2H	Slight interference fringe	o
" 4	"	220, 5	"		"
Use example 7	5 ~ 6	300, 1	3H	Uniform	"
" 8	"	220, 5	2H	"	"
" 9	15	300, 1	4H	"	"
" 10	"	220, 5	3H	"	"
" 11	24	300, 1	4H	"	Δ
" 12	"	220, 5	3H	"	o
" 13	30	220, 5	3H	"	Δ

Note: 1) Substrate: SUS 304 BA, 0.4 mm thick.

2) Application method: according to immersion method, and bar coater was used.

3) Coating material: prepared according to Coating material preparation example 1-1.

4) Setting conditions: temperature--temperature inside the furnace: time--time during which the material is retained inside the furnace.

5) Cross-cut, Erichsen's peel test: cross-cut in 1 mm mesh, Erichsen 5 mm extruded and subjected to peel test with cellophane tape.

o -- no peel; Δ -- slight peel.

As apparent from Table 3, when the coating thickness is less than 1 μ, an interference fringe is observed, and when it is 24 μ, a slight peel is observed in the cross-cut, Erichsen's cellophane peel test; thus the coating thickness was judged to be suitably in the range of 1 to 30 μ. Further, as to the setting conditions, it is apparent that a short time treatment such as 3 minutes at 220°C ~ one minute at 300°C affords a sufficient coating-formability.

Use examples 14 ~ 17 and Comparative examples 5 ~ 6

As the stainless substrate, SUS 304 DF (Dull Finish, satin texture) or HL (Hair Line Finish) was used; the thickness of coating material polished and baked was varied; and non-bent or 90° bent product was exposed to atmospheric air to compare the presence or absence of rust formation with that of a stainless substrate having no coating material applied thereon.

The test conditions and the results are shown in the following Table 4.

Table 4

Experi-ment No.	Kind of Substrate	Exposed days / Coating thickness / Bent or non-bent	20 days 8 µ	20 days 24 µ	60 days 8 µ	60 days 24 µ
Use ex. 14	SUS 304 DF	non-bent	o	o	o	o
" 15	"	Bent, 90°	"	"	"	"
" 16	SUS 304 HF	non-bent	"	"	"	"
" 17	"	Bent, 90°	"	"	"	"
Compar. ex. 5	SUS 304 DF	non-bent	-	×	-	×
" 6	SUS 304 HL	"	-	×	-	×

Note) Coating material: prepared according to Coating material preparation example 1-1.

Setting conditions: 220°C, 5 min.

Evaluation: o -- no rust, × -- rusted.

Non-coated SUS 304 DF and HL both rusted through 20 days' exposure.

As apparent from Table 4, the product of the present invention does not rust even under the conditions of exposure to atmospheric air where the substrate rusts, and the coating of the present invention retains rust-preventive function even through 90° bending processing.

Use examples 18 ~ 22 and Comparative example 7

As the stainless substrate, SUS 430 BA (0.5 mm thick) was used; as the coating material, the product obtained in Coating material preparation example 2-1 was used; and the setting conditions of the coating material of the present invention and the bending processability of the resulting coating depending on the coating thickness were observed.

Baking conditions and the presence or absence of abnormality at the R part of the resulting baked coating are shown in Table 5.

Table 5

Experiment No.	Baking temp.	time	90° 8 μ	90° 24 μ	180° 8 μ	180° 24 μ
Compar. ex. 7	200°C	10 min.	o	Δ	Δ	Δ
Use ex. 18	"	15 min.	o	o	o	o
" 19	250°C	3 "	o	Δ	Δ~o	Δ
" 20	"	5 "	o	o	o	o
" 21	300°C	2 "	o	o	o	o
" 22	"	5 "	o	o	o	o

(Header diagonal labels: Bent angle / Coating thickness)

Note) Judgement: After roll bending processing at R = 2t, R part was outwardly observed.

o: -- no abnormality, Δ: -- R part, slightly white-turbid, ×: -- R part, white-turbid.

As seen from Table 5, the coating of the present invention exhibits almost generally good results even in the case of 180° roll bending processing, and as to the heating time for baking, 10 minutes or more at 200°C, 3 minutes or more at 250°C and 2 minutes or more at 300°C were adequate, but a slight interference color was observed at a baking time of 8 minutes at 300°C; hence shorter than 8 minutes are preferred.

Use examples 23 ~ 26 and Comparative examples 8 ~ 9

As the substrate, SUS 430 BA or SUS 304 HL was used; as the coating material, products of coating material preparation examples 1-1 and 1-2, a commercially available acrylic resin and a product of oxidation method were used; baking was carried out varying the setting conditions and the coating thickness; and the performances of the resulting coated sheets directed to the following items were evaluated. The coating conditions and the results are shown in Table 6.

The evaluation method was conducted according to the following three-stage method:

o: Abnormalities such as peel, stain, crack, etc. were not observed at all.

Δ: Slight abnormalities were observed.

×: Abnormalities were clearly observed.

(1) Rust resistance: Artificial seawater spray (20°C. one minute) followed by infrared ray lamp drying were carried out and the resulting appearance was evaluated.

(2) Formability: 90° bending and 180° bending at R = 2t were carried out, and thereafter a cellophane tape peel test upon the resulting bent part was carried out; the resulting appearance was evaluated.

(3) Chemical resistance: Immersed in a mixed solution of 28% HCℓ and 3% H_2O_2 water for 30 seconds. The resulting appearance was evaluated.

(4) Saline solution resistance: Immersed in 3% NaCℓ aqueous solution kept at 50°C for 144 hours, followed by water-washing and thereafter a cellophane tape peel test. The resulting appearance was evaluated.

(5) Alkali resistance: Immersed in 0.5% NaOH aqueous solution kept at 50°C for 144 hours. The resulting appearance was observed.

(6) Coin scratch resistance: The surface of the coated sheet was injured with 10 yen coin, and the resistance was designated in a four-stage manner

(A (good) ~ D (bad)), depending on the extent of injury.

7 Trichlene resistance: Cotton cloth was immersed in trichloroethylene and the surface of the coated sheet was rubbed definite times with the cloth. The resulting appearance was evaluated.

8 Weather resistance: Test was carried out according to the accelerated weather resistance test of JIS K 5400, and the appearance and the degree of reflection ($Q = 60°$) were measured.

Table 6

	Use example				Compar. ex.	
	23	24	25	26	8	9
Substrate 1	BA	HL	BA	HL	HL	BA
Coating material 2	2-1	2-2	2-1	2-1	Acryl	Oxidation
Setting conditions 3 °C min.	①	②	②+	②+	④	
°C min.			③	③		
Coating thickness μ	5	6	5	6	20	0.1
Color tone appearance	Good	→	→	→	→	*
Pencil hardness H	5	3	5	5	2	3 ~ 9
Rust resistance: non-processed part	o	o	o	o	o	×
processed part, 90° bent	o	o	o	o	o	×
" , 180° bent	o	Δ	o	o	Δ	×
Formability: R = 90°	o	o	o	o	o	o
R = 180°	o	Δ	o	o	Δ	o
Chemical resistance	o	o	o	o	o	×
Saline solution: flat sheet	o	o	o	o	×	o
cross-cut	o	o	o	o	×	o
Alkali resistance: flat sheet	o	o	o	o	×	o
cross-cut sheet	o	o	o	o	×	o
Coin scratch resistance	B	C	A	A	B	A

Table 6 (continued)

	Use example				Compar. ex.	
	23	24	25	26	8	9
Trichlene resistance: rubbing 30 times	o	Δ	o	o	o	o
" 90 times	o	×	o	o	o	o
Weather resistance[4], appearance	o	o	o	o	×	o
2500 Hr degree of reflection	±	±	±	±	-4	±

Note) 1: BA and HL represent SUS 430 BA and SUS 304 HL, respectively.

2: 2-1, 2-2, acryl and oxidation represent Coating material examples 2-1, 2-2, acrylic resin and oxidation method, respectively.

3: 1, 2, 3 and 4 represent 6 min. at 250°C, 2 min. at 230°C, 20 min. at 220°C and 3 min. at 180°C, respectively.

4: ± represents no change and -4 represents 4% reduction in 600 hours.

*: Visual color tone changed.

CLAIMS

1. A thermoset acrylic resin composition for coating metallic materials, obtained by subjecting to radical copolymerization, the following monomers (a) to (d), where the percentages are by weight based on the total weight of the monomers (a) to (d) :

(a) at least one acrylic acid ester or methacrylic acid ester, with the ester having 1 to 12 carbon atoms in the ester group moeity, in an amount of 40 to 80% by weight;

(b) at least one hydroxyl group- or epoxy group-containing acrylic acid ester or hydroxyl group- or epoxy group-containing methacrylic acid ester, in an amount of 20 to 5% by weight;

(c) a vinyl group-containing polysiloxane, in an amount of 20 to 0.01% by weight; and

(d) a vinyl group-containing silane compound, in an amount of 20 to 2% by weight.

2. A composition according to claim 1 wherein 0.1 to 5% by weight of an organic acid having 3 or more carbon atoms is blended in with the mixture of the monomers.

3. A composition according to claim 2 wherein the organic acid is acrylic acid or maleic anhydride.

4. A composition according to claim 1, 2, or 3 wherein thecopolymer obtained by the radical copolymerization has a weight average molecular weight of 5,000 to 300,000.

5. A composition according to any preceding claim, wherein the vinyl group-containing polysiloxane is at least one of the following monomers (e) to (i):

(e) vinyl group-terminated polyalkylsiloxanes having a viscosity at 25°C (η) of 2 to 100,000 cp and the following structural formula:

$$CH_2=CH-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH=CH_2$$

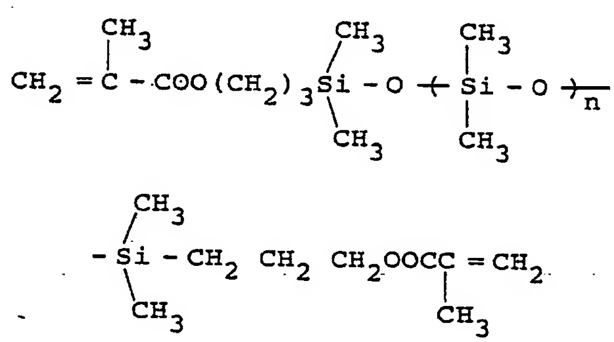
wherein n̲ represents a positive integer;

(f) polydimethyl-polymethylvinylsiloxane copolymers having a η of 10-100,000 cp at 25°C and the following structural formula

$$(CH_3)_3\,Si-O\left(\overset{CH=CH_2}{\underset{CH_3}{Si}}-O\right)_m\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O\right)Si(CH_3)_3$$

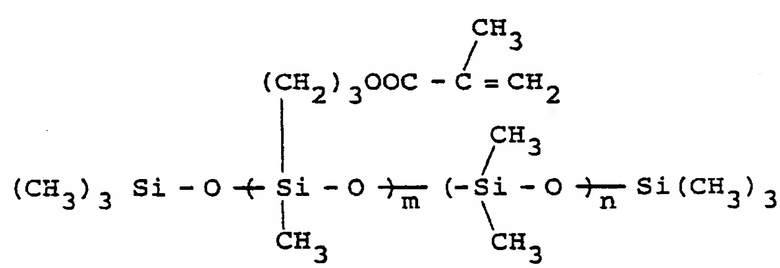
wherein m and n each represent a positive integer;

(g) methacryloxypropyl group-terminated polydimethylsiloxanes having a η of 5 to 100,000 cp and the following structural formula:



wherein n represents a positive integer;

(h) polydimethyl-methacryloxypropylmethylsiloxanes having a η of 10 to 100,000 cp and the following structural formula:



wherein n represents a positive integer; and

(i) compounds having a phenyl group substituted for some of $-(CH_3)_2$ in the $Si-(CH_3)_2$ groups in the compounds (e) to (h).

6. A stainless steel piece having thereon a coating comprising a modified acrylic resin as an active ingredient, prepared by subjecting to radical copolymerization, (1) 20 to 2% by weight of a vinyl group-containing alkoxysilane, (2) 20 to 0.01% by weight of a vinyl group-containing polysiloxane, (3) 20 to 5% by weight of a hydroxyl group- or epoxy group-containing acrylic acid ester or methacrylic acid ester and 40 to 80% by weight of (4) an acrylic acid ester having 1 to 12 carbon atoms in the ester group moiety or (5) a methacrylic acid ester having 1 to 12 carbon atoms in the ester group moiety, in the presence of 0.1 to 5% by weight of an organic acid having 3 or more carbon atoms, the respective % by weight being based on the total weight of the monomers (1) to (5), and baking at a temperature of 100° to 350°C.

7. A stainless steel piece according to claim 6 wherein the coating has a thickness of 1 to 30 µ.

8. A stainless steel piece according to claim 6 or 7 wherein a pigment having an average particle diameter of 2 µ or less is present in the coating.

9. A stainless steel piece according to claim 6, 7 or 8 wherein after shaping of the piece the coating is baked at a temperature of 100 to 300°C.

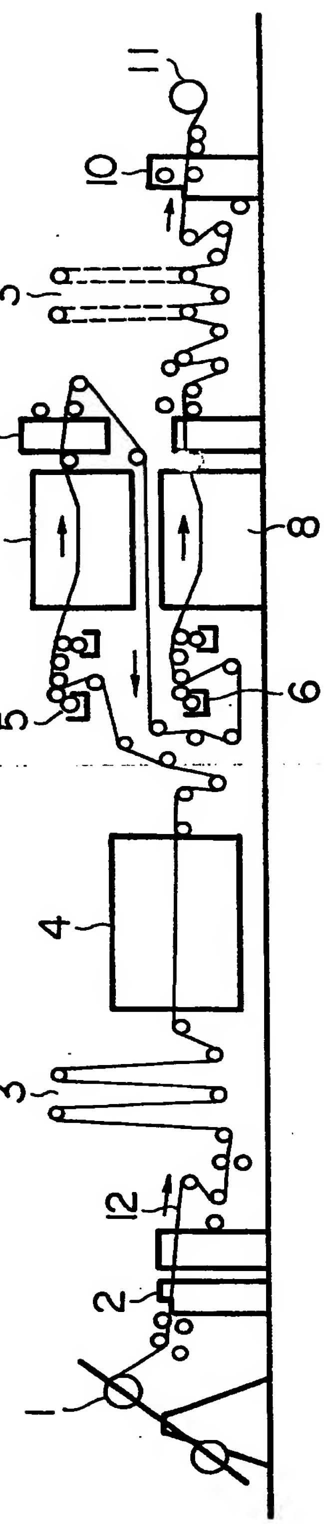


FIG. 1